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Analysis of aroma compounds of nine autochthonous and non-autochthonous loquat cultivars grown in Sicily

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PAPER

Abstract

Loquat cultivation in Sicily is mainly based on nonnative cultivars and local ecotypes characterized by high nutraceutical value and appreciable physicochemical characteristics. Increased interest in commercial loquat production has increased the intention to provide premium quality loquat cultivars that include volatile substances capable of conditioning the sensorial properties and, therefore, the acceptability of fruits by consumers. This study determined the content of volatile compounds in nonnative and local loquat fruits grown in Sicily. Analyses were performed on five international cultivars and four local cultivars.

Keywords: international and local cultivars, loquat, volatile compounds

Introduction

In recent years, there has been a growing demand for fruit products from tropical and subtropical countries. Among the attractive characteristics that fuel this demand from consumers is the increased interest in products with a high nutraceutical value, importantly their characteristic taste and flavour (Gentile *et al.*, 2019). It is well known that the taste and quality of food are determined by aromatic compounds, which in turn, influence consumer preferences and attract the attention of farmers who require more information and analytical tools to enable them to select the most suitable cultivars to grow (Baldwin, 2004; Schwab *et al.*, 2008). The aroma is a critical quality parameter that differentiates one fruit from the other and it is associated with many volatile compounds (Lo Bianco *et al.*, 2010; Ye *et al.*, 2017; Yuan *et al.*, 2018) belonging to different chemical groups, such as esters, alcohols, terpenes, ethers, aldehydes, etc.

One of the fruits belonging to the subtropical species, which is well adapted to the temperate zones of the Mediterranean and whose production is concentrated in Spain and Italy, is the Loquat (*Eriobotrya japonica* Lindl). It is an evergreen subtropical species (Family Rosaceae - Subfamily Mathat loideae) that originates from Southern China. Today, 90% of the cultivation is concentrated in the region of Sicily, particularly in the province of Palermo (Farina *et al.*, 2016), with an extended harvest period (from April to June) based on several cultivars and local ecotypes (Farina *et al.*, 2011; Gentile *et al.*, 2016). Loquat cultivation in Sicily is based especially on nonnative cultivars and local ecotypes characterized by a high nutraceutical value (Gentile *et al.*, 2019) and appreciable physico-chemical characteristics. Today, the interest in loquat commercial production has risen, and it is geared towards loquat cultivars of premium quality (Badenes *et al.*, 2013). The most important characteristic for the market is fruit size. The value of the crop (Goulas *et al.*, 2014) is in line with the commercial classification (Testa *et al.*, 2020). As a result, fruits are divided into four classes based on their diameter: GGG for fruits over 53 mm; GG for fruits between 46 and 52 mm; G for fruits between 32 and 45 mm; and M for fruits between 31 and 28 mm. Quality is a complex of chemical and physical parameters and aromatic composition. Volatile flavor compounds are likely to play a key role in determining the perception and acceptability of products by consumers (Pott *et al.*, 2020). Fruits produce a range of volatile compounds that make up their characteristic aromas and contribute to their flavor. The differences in volatile compounds may be because of their ripening phase during the harvest time (Agozzino *et al.*, 2007) and differences in the studied cultivars (Farina *et al.*, 2020). Many studies on the volatile component of many fruits can be found in literature, while only a few studies have been conducted to date for the Mediterranean loquat. In this regard, Shaw and Wilson (1982) identified the following volatile compounds in loquat fruits; 2-phenylethanol, 3-hydroxy-2-butanone, phenylacetaldehyde, isomeric hexen-1-ols, ethyl acetate, methyl cinnamate, and β-ionone. Hexanal and (E)-2-hexenal and benzaldehyde have also been identified by Fröhlich and Schreier (1990). Chen *et al.* (2011) reported that β-ionone, decanoic acid, propanoic acid, bicycle nonane, and heptadecane are the major volatile compounds in the Zaozhong 6 cultivar. These studies highlighted that volatile compounds such as 2E-hexenol, 3Z-hexenol, and hexanol contribute to green notes; methyl cinnamate and eugenol contribute to the spicy note; ethyl and methyl 2-methylbutanoates are responsible for fresh fruity notes; a sweet watery aroma was also detected by traces amount of phenylacetaldehyde, vanillin, and β-ionone (Hideki *et al.* 1998). Finally, Takahashi *et al.* (2000) reported that the Tanaka cultivar presents phenylacetaldehyde as the most aromatic compound, while small traces of hexanal, (E)-2-hexanal, hexanoic acid, and β-ionone have also been found. Nevertheless, many other volatile compounds are present in traces which can be detected not only by analytical instruments but also by human olfaction (Goff *et al.*, 2006).

The aim of this study was to determine for the first time the content of volatile compounds in non-native and local loquat fruits grown in Sicily.

Material and Methods

Plant material

Two hundred and seventy loquat fruits (*Eriobotrya japonica* Lindl.) were harvested in an experimental orchard located in Santa Maria di Gesù (Palermo, Italy, 38°04'N, 13°22'E, 150 m a.s.l.) between April and June at commercial ripening, using fruit peel color as a ripening index (807-809 degree of Biologische Bundesantalt, Bundessortenamt and Chemische Industrie (BBCH) Scale). The analyses were carried out on four local cultivars (BRT20, Claudia, Sanfilippara, and Nespolone di Trabia) and five international cultivars (Algerie, Bueno, El Buenet, Golden Nugget, and Peluche). A sample of 30 fruits per cv was submitted for laboratory analyses.

Commercial classification

Primarily the loquat fruits were divided into international and local cultivars and later were classified based on the flesh color (yellow and white) and diameter (GGG, GG, G, and M), according to Testa *et al.* (2020).

Volatile compounds analysis

Three replicates of the pulp (about 200 g) of 10 fruits were separated from the peel and seeds with the addition of 100 mg of sodium metabisulfite. The pulps were crushed with a laboratory blender by a high-speed Ultra-Turrax T25 (IKA Labortechnik, Staufen, Germany) and centrifuged twice at 4500gand 4°C for 15 minutes and later the solid residue was washed with 70 mL of ethanol:water solvent (12:88). The final extract (250 mL) was then clarified with 0.1 g of the pectolytic enzyme without secondary glycosidase activity (Rapidase X-Press, DSM, The Netherlands) at room temperature for 2 hours. 1-Heptanol was added as internal standard (0.2 mL of 40 mg/L in 10% ethanol) to the samples and was loaded onto a 5-g C18 reversed-phase solid-phase extraction (SPE) cartridge (Isolute, SPE Columns, Uppsala, Sweden), previously activated with 20 mL of methanol,50 mL of deionized water using a flow-rate of ca. 3 mL/min, and then rinsed with 100 mL of deionized water to eliminate sugars, acids, and other low molecular weight polar compounds. The free aromatic fraction was then eluted with 25 mL of dichloromethane. The eluate was dried over anhydrous sodium sulfate (Na_2SO_4) and was concentrated to about 0.2 mL under a stream of nitrogen. This extract, containing free volatile compounds, was immediately analyzed by gas chromatography/mass spectrometry (GC/MS). Then, the glycoconjugates aromas were finally eluted from the cartridge with 20 mL of methanol, and the eluate was concentrated to dryness using a vacuum rotary evaporator set at 30 °C (Buchi R-210, Switzerland). These dried glycosides extract were dissolved in 5 mL of citrate-phosphate buffer (0.2 M, pH 5) and subjected to enzymatic hydrolysis with 50 mg of an AR-2000 commercial preparation with glycosidase side activities (DSM Oenology, The Netherlands) at 40 °C for 24 hours. Later, 0.2 mL of 1-heptanol was added as internal standard, and the volatiles generated by the enzymatic hydrolysis of glycosylated precursors were then extracted following the SPE method previously described. The dichloromethane extract obtained was dried using anhydrous Na_2SO_4, concentrated to 0.2 mL, and kept at −20 °C until further analysis. GC/MS analysis was performed with an Agilent 6890 Series GC system and Agilent 5973 Network Mass Selective Detector (Agilent Technologies, Palo Alto, CA) equipped with a DB-WAX column (30 m, 0.250 mm i.d., film thickness 0.25 μm; Agilent Technologies).

The GC-MS conditions used were as reported by Corona *et al.* (2019). The detection was carried out by electron impact mass spectrometry in total ion current (TIC) mode using ionization energy of 70 eV. The mass acquisition range was m/z 30–330. Volatile organic compounds were identified by comparing their mass spectra and GC retention times with those of the pure commercial standard compounds and those within the NIST/EPA/NIH Mass Spectral Library database (Version 2.0d, build 2005). The concentration (μg/kg pulp) of volatile compounds was determined as 1-heptanol equivalents.

All solvents and reagents were purchased from WWR International (Milan, Italy).

Statistical analysis

The data were presented as mean ± standard deviation and analysed using the Tukey test at P ≤ 0.05. All statistical analysis was conducted using XLSTAT software version 9.0 (Addinsoft, Paris, France).

Results And Discussion

Commercial classification

According to commercial classification, our data showed that local ecotypes sizes were larger than international ecotypes (Amorós *et al.*, 2003; Testa *et al.,* 2020). However, only Peluche had the highest value as a well-known large fruit cultivar (Barone *et al.*, 2010).

Varieties with a larger size are more appreciated by consumers because of their small portion size and high sugar/acid ratio. (Agusti *et al.* 2000; Testa*et al.* 2020). More sugar in local fruits versus international cultivars shows an increased degree of acidity (Gentile *et al.,* 2016).

In this study, all the international cultivars had yellow flesh, whereas, among the local cultivars, only Nespolone di Trabia showed more similar behavior with that of the international cultivars (yellow flesh). On the other hand, BRT 20, Claudia, and Sanfilippara, showed white flesh with highest commercial classification (Table 1).

Table 1. Commercial classification based on origin, size, and color of analyzed loquat fruits: GGG> 53mm, GG 46-52mm, G 32-45 mm, and M 31-28 mm.

Origin	Cultivars	Commercial classification	Color classification
Local	BRT 20	GGG	White flesh
	Claudia	GGG	White flesh
	Sanfilippara	GG	White flesh
	Nespolone di trabia	GG	Yellow flesh
International	Algerie	GG	Yellow flesh
	Bueno	G	Yellow flesh
	El buenet	G	Yellow flesh
	Golden nugget	GG	Yellow flesh
	Peluche	GGG	Yellow flesh

Volatile compounds analysis

GC-MS analysis of the concentrated flesh extract of SPE was performed to evaluate the aromatic compounds of loquat fruit flesh, and 35 free volatile compounds (Table 2) and 17 glycosylated compounds (Table 3) were detected. Of which, 14 were acids, 10 alcohols, two aldehydes, one benzenoid, and eight esters. Among which four were terpenes, four C13-norisoprenoids, and nine benzenoids. The latter were released after enzymatic hydrolysis from aromatic precursors linked to sugars.

During maturation, the volatile compounds of the two cultivars, Algerie and Golden nugget, have been studied, and a strong similarity was identified in terms of aroma, flavor, and parameters related to physiological-qualitative traits (Pino *et al.,* 2002; Besada *et al.*, 2013, 2017).

The heritability of loquat aromas was assessed by Jiang *et al.* (2014) by examining the composition of the volatile compounds of Xiantgtian and Jiefangzhong cultivars and two-hybrid progenies (Xiangzhong No.11 and Zhongxiang No. 25). They concluded that the level of volatile compounds in the fruit of the progeny was like the values known in their parents. Previous studies showed that the maturity stage determines the qualitative and quantitative volatile substances of many fruit species (Mattheis *et al.* 1992; Perez *et al.* 1992), for loquat, very little is known about their association with other ripening or quality characteristics that vary between cultivars (Jiang *et al.*, 2014).

Free volatile compounds

Among the free volatile compounds, minimal presence of volatile compounds that can characterize the aroma of loquat fruit was observed. It is a predominance of compounds belonging to the class of acids and alcohols, followed by esters, aldehydes, and finally a benzenoid

Table 2. Free volatile compounds released by enzymatic hydrolysis of glycosylated precursors (μg/kg pulp).

Compounds	Local cultivars*				International cultivars*				
	BRT 20	Claudia	Sanfilippara	Nespolone di trabia	Algerie	Bueno	El buenet	Golden Nugget	Peluche
Acids									
Butyric acid	4.0 ± 0.0	6.2 ± 0.1	0.6 ± 0.0	0.7 ± 0.1	0.4 ± 0.1	3.6 ± 0.2	6.4 ± 0.4	n.d.	0.5 ± 0.1
Pentanoic acid	10.3 ± 1.6	7.2 ± 0.1	3.5 ± 0.1	9.4 ± 0.3	8.1 ± 0.7	5.5 ± 0.5	15.7 ± 1.8	8.9 ± 0.7	8.5 ± 0.7
Hexanoic acid	1060.9 ± 44.7^{b}	1190.9 ± 31.0^{b}	554.4 ± 34.3^{a}	511.1 ± 29.4^{a}	475.2 ± 57.6^{ab}	645.8 ± 49.3^{ab}	358.4 ± 7.3^{a}	598.5 ± 50.4^{ab}	506.1 ± 34.9^{ab}
Heptanoic acid	2.2 ± 0.6^{b}	2.2 ± 0.2^{b}	2.2 ± 0.1^{b}	0.8 ± 0.0^{a}	0.1 ± 0.0^{a}	3.4 ± 0.2^{b}	3.8 ± 0.2^{b}	0.8 ± 0.0^{a}	0.4 ± 0.0^{a}
Octanoid acid	13.6 ± 1.3^{b}	11.9 ± 1.1^{b}	9.9 ± 0.1^{a}	11.9 ± 0.2^{b}	13.8 ± 2.0^{b}	10.5 ± 1.6^{ab}	12.1 ± 0.7^{ab}	4.2 ± 0.2^{a}	10.1 ± 0.7^{ab}
Nonanoic acid	18.4 ± 1.7^{b}	17.4 ± 1.9	17.4 ± 0.7	16.4 ± 1.2	13.2 ± 1.5	20.4 ± 1.5	18.9 ± 1.8	20.8 ± 1.3	19.0 ± 1.5
Decanoic acid	16.8 ± 1.0^{b}	8.0 ± 0.1^{a}	8.2 ± 0.5^{a}	17.4 ± 0.2^{b}	33.5 ± 1.3^{b}	12.0 ± 0.7^{a}	8.0 ± 0.3^{a}	20.1 ± 0.8^{ab}	11.4 ± 1.1^{a}
Dodecanoic acid	3.9 ± 0.1^{a}	2.4 ± 0.3^{a}	4.2 ± 0.1^{a}	9.9 ± 0.1^{b}	13.3 ± 0.8^{ab}	8.4 ± 0.6^{ab}	39.1 ± 3.6^{b}	12.8 ± 0.2^{ab}	4.4 ± 0.1^{a}
Tetradecanoic acid	7.5 ± 0.1	1.9 ± 0.2	3.7 ± 0.2	3.2 ± 0.0	7.4 ± 0.4	14.1 ± 1.4	15.6 ± 1.2	6.7 ± 0.7	1.8 ± 0.2
Pentadecanoic acid	7.6 ± 0.3^{a}	19.8 ± 1.2^{b}	15.9 ± 0.2^{b}	45.3 ± 1.0^{c}	4.0 ± 0.0^{a}	10.8 ± 0.8^{abc}	5.3 ± 0.2^{ab}	25.9 ± 0.1^{d}	1.3 ± 0.1^{a}
Hexadecanoic acid	240.6 ± 17.4^{a}	219.4 ± 21.1^{a}	444.9 ± 95.5^{b}	341.7 ± 21.3^{b}	636.4 ± 16.0^{b}	667.6 ± 26.8^{b}	617.8 ± 13.7^{b}	525.0 ± 10.5^{ab}	105.0 ± 4.2^{a}
Heptadecanoic acid	4.3 ± 0.2	n.d.	0.3 ± 0.0	2.1 ± 0.1	5.4 ± 0.1	3.4 ± 0.1	3.8 ± 0.3	1.5 ± 0.1	n.d.
Octadecanoid acid	124.5 ± 11.6	120.3 ± 10.2	133.4 ± 21.7	116.1 ± 4.8	143.4 ± 4.2^{b}	171.7 ± 12.0^{b}	137.0 ± 10.3^{b}	118.8 ± 13.7^{b}	73.9 ± 2.6^{a}
Benzoic acid	1053.3 ± 53.0^{b}	1185.2 ± 130.4^{b}	547.8 ± 33.5^{a}	504.5 ± 25.7^{a}	464.2 ± 55.2^{ab}	640.5 ± 61.0^{ab}	353.6 ± 7.9^{a}	594.4 ± 40.2^{ab}	502.8 ± 35.2^{ab}
Total	2567.8 ± 133.6^{b}	2792.8 ± 197.9^{b}	1746.3 ± 187.0^{a}	1590.6 ± 84.4^{a}	1818.4 ± 138.9^{ab}	2217.4 ± 157.7^{ab}	1595.3 ± 49.7^{ab}	1938.4 ± 118.9^{ab}	1245.2 ± 81.4^{a}
Alcohols									
1-Pentanolo	2.4 ± 0.0^{b}	2.9 ± 0.1^{b}	1.6 ± 0.1^{a}	2.7 ± 0.0^{b}	1.7 ± 0.1^{ab}	1.7 ± 0.1^{ab}	5.6 ± 0.2^{b}	2.7 ± 0.0^{ab}	4.3 ± 0.2^{ab}
3-Heptanol	0.6 ± 0.0	n.d.	0.4 ± 0.0	n.d.	0.3 ± 0.0^{a}	0.7 ± 0.0^{a}	2.8 ± 0.1^{b}	n.d.^{a}	0.2 ± 0.0^{a}
2-Hexanol	1.3 ± 0.0	n.d.	0.4 ± 0.0	1.6 ± 0.0	1.3 ± 0.1^{a}	54.7 ± 4.3^{b}	6.3 ± 0.2^{ab}	1.3 ± 0.1^{a}	2.0 ± 0.1^{a}
1-Hexanol	1.5 ± 0.0^{a}	1.4 ± 0.0^{a}	4.7 ± 0.1^{b}	5.5 ± 0.0^{b}	12.4 ± 0.3^{b}	2.0 ± 0.0^{a}	3.9 ± 0.1^{a}	3.5 ± 0.1^{a}	3.3 ± 0.2^{a}
3-Ethyl-3-heptanol	0.3 ± 0.0	n.d.	n.d.	n.d.	n.d.	0.2 ± 0.0	0.2 ± 0.0	n.d.	0.3 ± 0.1
Cis-3-hexen-1-ol	2.0 ± 0.0^{a}	12.5 ± 0.1^{bc}	6.7 ± 0.1^{b}	22.2 ± 1.2^{c}	20.0 ± 1.4^{ab}	5.9 ± 0.3^{ab}	2.8 ± 0.1^{a}	5.7 ± 0.2^{ab}	4.8 ± 0.0^{ab}
2-Butoxyethanol	5.4 ± 0.0^{b}	3.4 ± 0.1^{a}	3.5 ± 0.0^{a}	2.4 ± 0.0^{a}	5.0 ± 0.1^{ab}	3.9 ± 0.1^{ab}	2.0 ± 0.0^{a}	2.3 ± 0.1^{ab}	3.3 ± 0.3^{ab}
Trans-3-hexen-1-ol	2.7 ± 0.0^{a}	6.5 ± 0.1^{b}	4.0 ± 0.0^{a}	9.4 ± 2.6^{b}	26.5 ± 0.3^{c}	11.2 ± 0.2^{ab}	8.1 ± 0.1^{ab}	7.5 ± 0.2^{ab}	14.6 ± 0.2^{b}
2-Ethyl hexanol	5.3 ± 0.0	2.4 ± 0.0	3.9 ± 0.1	2.3 ± 0.0	5.6 ± 0.2	4.7 ± 0.2	2.5 ± 0.1	3.3 ± 0.1	2.8 ± 0.1

Total	21.6 ± 0.0^{a}	29.1 ± 0.4^{a}	25.4 ± 0.4^{a}	46.2 ± 3.9^{b}	72.5 ± 2.5^{c}	85.1 ± 5.1^{bc}	34.2 ± 0.9^{abc}	26.5 ± 0.8^{abc}	35.6 ± 1.2^{abc}
Aldehydes									
Cis-2-hexenal	6.2 ± 0.1^{a}	8.7 ± 0.1^{a}	9.2 ± 0.2 ^{a}	20.5 ± 0.2^{b}	92.1 ± 8.9^{b}	7.9 ± 0.6^{a}	n.d.^{a}	5.0 ± 0.1^{a}	30.3 ± 1.7^{ab}
Nonanal	1.6 ± 0.0 ^{ab}	3.5 ± 0.1^{b}	2.4 ± 0.1^{ab}	1.0 ± 0.0^{ab}	0.6 ± 0.0^{a}	1.8 ± 0.1^{ab}	0.4 ± 0.0^{a}	1.4 ± 0.2^{ab}	1.3 ± 0.2^{ab}
Total	7.8 ± 0.1^{a}	12.3 ± 0.2^{ab}	11.6 ± 0.3^{ab}	21.5 ± 0.2^{b}	92.7 ± 8.9^{b}	9.7 ± 0.7^{ab}	0.4 ± 0.0^{a}	6.4 ± 0.3^{a}	31.6 ± 1.9^{ab}
Benzenoids									
Vanillin	11.7 ± 0.2^{b}	8.7 ± 0.1^{a}	8.0 ± 0.1^{a}	8.2 ± 0.0^{a}	11.1 ± 1.1^{ab}	27.9 ± 2.4^{b}	n.d.^{a}	11.8 ± 0.2^{ab}	10.1 ± 0.1^{ab}
Esters									
Ethyl hexanoate	1.9 ± 0.1^{a}	n.d.^{a}	5.0 ± 0.1^{ab}	0.6 ± 0.0^{a}	3.3 ± 0.5^{a}	3.8 ± 0.4^{a}	9.6 ± 0.3^{b}	1.0 ± 0.0 ^{a}	3.2 ± 0.2^{a}
Ethyl octanoate	3.4 ± 0.0^{a}	1.4 ± 0.0^{a}	9.4 ± 0.3^{a}	3.7 ± 0.0^{a}	11.3 ± 1.8^{a}	6.7 ± 0.3^{a}	25.2 ± 0.3^{b}	3.1 ± 0.2^{a}	7.4 ± 0.2^{a}
Ethyl-3-hydroxy butyrate	230.8 ± 8.7^{d}	10.0 ± 0.1^{a}	181.1 ± 9.6^{cd}	7.1 ± 0.1^{a}	83.3 ± 4.5^{b}	203.9 ± 23.1^{d}	120.8 ± 10.8^{c}	5.2 ± 0.3^{a}	4.6 ± 0.0^{a}
Ethyl decanoate	0.2 ± 0.0^{a}	0.2 ± 0.0^{a}	1.3 ± 0.0^{ab}	1.2 ± 0.0^{ab}	2.8 ± 0.2^{b}	0.5 ± 0.0^{a}	2.4 ± 0.1^{b}	0.6 ± 0.0^{a}	0.5 ± 0.1^{a}
Diethyl succinate	0.8 ± 0.0^{a}	n.d.^{a}	1.3 ± 0.1^{ab}	0.1 ± 0.0^{a}	3.3 ± 0.1^{b}	0.7 ± 0.0^{a}	0.3 ± 0.0^{a}	0.2 ± 0.0^{a}	2.5 ± 0.1^{b}
Butanoic Acid-2-methyl	137.4 ± 10.9^{a}	118.7 ± 9.1^{a}	8.7 ± 0.1^{a}	65.7 ± 1.8^{a}	623.9 ± 7.1^{c}	415.1 ± 36.2^{b}	308.0 ± 28.6^{b}	7.3 ± 0.2^{a}	301.3 ± 3.8^{b}
Hexadecanoic acid methyl ester	4.4 ± 0.4^{a}	25.3 ± 0.2^{b}	2.7 ± 0.2^{a}	7.4 ± 0.2^{a}	4.3 ± 0.3^{a}	4.6 ± 0.3^{a}	2.9 ± 0.1^{a}	1.6 ± 0.1^{a}	6.4 ± 0.2^{b}
Hexadecanoic acid ethyl ester	1.6 ± 0.0	2.6 ± 0.0	1.4 ± 0.1	2.4 ± 0.2	7.0 ± 0.3	1.5 ± 0.1	5.4 ± 0.2	2.4 ± 0.2	2.8 ± 0.1
Total	380.5 ± 20.1^{cd}	158.2	210.9 ± 10.5^{abc}	88.1 ± 2.3^{a}	739.3 ± 14.8^{c}	636.7 ± 60.4^{c}	474.7 ± 40.4^{b}	21.5 ± 1.0^{a}	328.8 ± 4.7^{b}

*Mean ± standard deviation (n = 3). Different superscripted letters indicate significant differences for $P \leq 0.05$ (analysis of variance or Tukey test).
n.d., not determinable.

Table 3. Glycosylated volatile compounds released by enzymatic hydrolysis of glycosylated precursors (μg/kg pulp).

	Local cultivars*				International cultivars*				
Compounds	**BRT 20**	**Claudia**	**Sanfilippara**	**Nespolone d' trabia**	**Algerie**	**Bueno**	**El buenet**	**Golden nugget**	**Peluche**
Terpenes									
Trans-8-diidrolinalool	6.1 ± 0.0^{b}	8.0 ± 0.1^{b}	4.0 ± 0.0^{a}	3.3 ± 0.0^{a}	10.7 ± 0.2^{c}	6.9 ± 0.0^{b}	3.4 ± 0.1^{ab}	6.1 ± 0.2^{b}	1.4 ± 0.0^{a}
Trans-8-hydroxylinalool	5.5 ± 0.1^{a}	15.1 ± 0.3^{b}	7.0 ± 0.2^{a}	15.5 ± 0.3^{b}	12.8 ± 0.1^{bc}	9.5 ± 0.2^{b}	7.1 ± 0.2^{b}	16.0 ± 1.4^{c}	1.0 ± 0.0^{a}
Cis-8-hydroxylinalool	1.5 ± 0.0^{a}	4.1 ± 0.1^{ab}	8.5 ± 0.2^{b}	7.6 ± 0.3^{b}	3.2 ± 0.0^{b}	4.3 ± 0.2^{bc}	5.7 ± 0.1^{c}	3.7 ± 0.2^{b}	1.1 ± 0.0^{a}
Geranial	3.4 ± 0.0^{ab}	2.6 ± 0.2^{a}	6.9 ± 0.2^{b}	4.2 ± 0.2^{ab}	6.0 ± 0.0^{bc}	3.8 ± 0.1^{a}	4.8 ± 0.1^{b}	7.6 ± 0.2^{c}	5.6 ± 0.2^{b}
Total	16.5 ± 0.1^{a}	29.8 ± 0.7^{b}	26.4 ± 0.6^{b}	30.6 ± 0.8^{b}	32.7 ± 0.3^{c}	24.5 ± 0.5^{b}	21.1 ± 0.5^{b}	33.4 ± 2.0^{c}	9.2 ± 0.2^{a}
C13-norisoprenoids									
3-oxo-a-ionol	59.2 ± 4.8^{a}	62.4 ± 1.2^{a}	94.4 ± 4.9^{ab}	207.5 ± 23.0^{b}	461.0 ± 41.5^{d}	286.6 ± 19.8^{c}	217.9 ± 19.3^{b}	373.4 ± 34.0^{c}	112.3 ± 9.8^{a}
3-4-dihydro-3-oxo-a-ionol	19.8 ± 1.1^{a}	41.9 ± 1.1^{ab}	32.7 ± 2.9^{ab}	74.1 ± 14.0^{b}	92.1 ± 7.2^{c}	55.6 ± 4.2^{b}	27.7 ± 2.0^{a}	72.9 ± 17.1^{bc}	24.8 ± 1.1^{a}
3-OH-b-ionone	2.0 ± 0.0^{a}	28.5 ± 1.3^{ab}	34.1 ± 1.6^{b}	64.7 ± 3.7^{c}	23.4 ± 2.9^{c}	13.0 ± 1.8^{bc}	7.8 ± 1.0^{ab}	22.2 ± 1.6^{c}	2.6 ± 0.1^{a}
Vomifoliol	135.0 ± 10.4^{a}	149.2 ± 0.8^{a}	178.0 ± 12.2^{a}	283.4 ± 23.8^{b}	581.6 ± 26.7^{c}	79.9 ± 2.2^{a}	101.2 ± 9.1^{a}	283.8 ± 10.9^{b}	120.0 ± 11.5^{a}
Total	215.9 ± 16.3^{a}	281.9 ± 4.4^{ab}	339.2 ± 21.6^{b}	629.6 ± 64.5^{c}	1158.1 ± 78.3^{c}	435.1 ± 28.0^{ab}	354.5 ± 31.4^{a}	752.3 ± 63.6^{bc}	259.7 ± 22.5^{a}
Benzenoids									
Eugenol	32.3 ± 1.6^{a}	21.7 ± 0.1^{b}	15.9 ± 0.2^{a}	27.9 ± 0.3^{b}	55.0 ± 3.6^{b}	59.2 ± 4.1^{b}	24.7 ± 1.9^{a}	121.3 ± 9.5^{c}	16.1 ± 0.2^{a}
4-vinylguaiacol	54.4 ± 4.1^{c}	35.2 ± 0.3^{b}	30.1 ± 0.2^{a}	32.5 ± 0.4^{a}	29.0 ± 2.4^{a}	25.1 ± 2.1^{a}	21.4 ± 0.7^{a}	78.0 ± 8.4^{b}	16.9 ± 0.9^{a}
Isoeugenol	2.6 ± 0.1^{a}	7.3 ± 0.1^{b}	7.9 ± 0.1^{b}	5.2 ± 0.1^{a}	23.0 ± 0.1^{c}	22.0 ± 1.0^{c}	24.5 ± 1.5^{d}	10.8 ± 0.7^{ab}	7.0 ± 0.1^{a}
Methylvanillate	30.5 ± 0.2^{a}	192.5 ± 11.9^{b}	24.7 ± 0.2^{a}	45.1 ± 0.4^{a}	194.9 ± 10.7^{c}	32.0 ± 2.9^{a}	19.8 ± 1.7^{a}	134.8 ± 0.4^{b}	11.8 ± 0.2^{a}
Benzylalcohol	5.9 ± 0.2^{a}	7.9 ± 0.2^{a}	6.8 ± 0.1^{a}	12.2 ± 0.2^{b}	11.3 ± 1.1^{c}	3.4 ± 0.2^{ab}	4.8 ± 0.2^{b}	12.2 ± 0.1^{c}	2.5 ± 0.1^{a}
2-phenylethanol	225.4 ± 13.6^{b}	443.8 ± 24.3^{c}	177.4 ± 13.7^{a}	234.1 ± 21.1^{b}	285.1 ± 18.7^{c}	92.4 ± 2.1^{b}	84.7 ± 2.0^{b}	241.7 ± 13.0^{c}	77.2 ± 6.2^{a}
Vanillin	18.8 ± 0.2^{c}	13.8 ± 0.7^{b}	3.9 ± 0.2^{a}	13.4 ± 1.8^{b}	12.4 ± 0.8^{ab}	10.2 ± 1.0^{ab}	9.1 ± 0.7^{ab}	25.4 ± 2.3^{c}	2.8 ± 0.1^{a}
Methoxyeugenol	5.7 ± 0.2^{b}	5.3 ± 0.1^{b}	3.9 ± 0.1^{a}	2.2 ± 0.2^{a}	2.3 ± 0.0^{b}	3.4 ± 0.1^{c}	5.6 ± 0.3^{d}	0.4 ± 0.0^{a}	3.8 ± 0.1^{c}
Syringaldehyde	56.3 ± 0.4^{ab}	4.6 ± 0.1^{a}	45.9 ± 2.2^{ab}	36.8 ± 3.2^{ab}	68.7 ± 3.4^{b}	16.7 ± 0.9^{ab}	26.3 ± 1.9^{ab}	10.2 ± 0.7^{ab}	7.0 ± 1.0^{a}
Total	431.9 ±20.6^{b}	732.3 ± 37.8^{c}	316.5 ± 17.0^{a}	409.4 ± 27.7^{b}	681.7 ± 40.8^{c}	264.3 ± 14.4^{ab}	221.0 ± 10.9^{ab}	634.8 ± 35.1^{c}	145.1 ± 8.9^{a}

*Mean ± standard deviation (n=3). Different superscripted letters indicate significant differences for $P \leq 0.05$ (analysis of variance or Tukey test). n.d., not determinable.

(vanillin only, according to Hideki *et al.* 1998). The identified acids range from C4 to C18, the esters from C4 to C10 and C16; they contribute to the taste sensations perceptible in the mouth during tasting and eating of the flesh, giving taste, fat sensation, and different aromatic sensations, ranging from fruity to floral (Table 4). The greater acids concentration are: hexanoic (1060.9±44.7 in BRT20, local cultivar), benzoic (1185.2 mg/kg flesh fruit in Claudia, local cultivar), hexadecanoic (667.6 mg/kg flesh fruit in Bueno, international cultivar), and octadecanoic (171.7 mg/kg flesh fruit also in Bueno cultivar).

In terms of bad tastes, the highest values of butyric and decanoic acid, commonly detectable in cheese and fat

Table 4. Odor descriptor and odor threshold volatile compounds.

Compounds	Odor descriptor	Odour threshold (ppb)	Reference
Acids			
Butyric acid	Rancid, cheese	173	Fariña *et al.* (2015)
Pentanoic acid	Sweet	70	Pino and Mesa (2006)
Hexanoic acid	Fatty, cheese	420	Fariña *et al.* (2015)
Heptanoic acid	Waxy, cheese, fruity	–	www.thegoodscentscompany.com/
Octanoic acid	Fatty, cheese	500	Fariña *et al.* (2015)
Nonanoic acid	Green, fatty	3000	Pino and Mesa (2006)
Decanoic acid	Rancid, fatty	1000	Fariña *et al.* (2015)
Dodecanoic acid	Fatty, waxy	–	www.thegoodscentscompany.com/
Tetradecanoic acid	Waxy, oily, fatty	–	www.thegoodscentscompany.com/
Pentadecanoic acid	Waxy	–	www.pherobase.com
Hexadecanoic acid	Oily	–	www.pherobase.com
Heptadecanoic acid	Oily	–	www.pherobase.com
Octadecanoid acid	Oily	–	www.pherobase.com
Benzoic acid	Balsamic	–	
Alcohols			
1-Pentanol	Green, grassy, powerful	4,000	Pino and Mesa (2006)
3-Heptanol	Herbal	–	www.thegoodscentscompany.com/
2-Hexanol	Chemical, winey	500	Pino and Mesa (2006)
1-Hexanol	Fatty, green, resin, flower, sweet	500	Bonneau *et al.* (2016)
3-Ethyl-3-heptanol		–	
cis-3-hexen-1-ol	Green, moss, fresh	110	Bonneau *et al.* (2016)
2-butoxyethanol		–	
trans-3-hexen-1-ol	Green, grass, fruity	70	Bonneau *et al.* (2016)
2-Ethyl-hexanol	Oily, rose, sweet	–	Li *et al.* (2011)
Aldehydes			
Trans-2-hexenal	Green, banana-like	17	Pino and Mesa (2006)
Nonanal	Fatty, citrus, green, floral, sweet, soapy	1	Bonneau *et al.* (2016)
Benzenoid			
Vanillin	Vanilla-like, sweet	25	Bonneau *et al.* (2001)
Esters			
Ethyl hexanoate	Apple peel, fruity	1	Pino and Mesa (2006)
Ethyl octanoate	Fruity, fat	194	Pino and Mesa (2006)
Ethyl-3-hydroxy butyrate	Fruity, grape	1000	Moyano *et al.* (2002)
Ethyl decanoate	Sweet, oily, nutlike, grape	6300	Pino and Mesa (2006)
Diethyl succinate	Overripe melon, lavender	100,000	Fariña *et al.* (2015)
2-methylbutanoic acid	Cheese	250	Fariña *et al.* (2015)
Methyl hexadecanoic	Waxy	–	www.thegoodscentscompany.com/
Ethyl hexadecanoic	Waxy	–	www.thegoodscentscompany.com/

notes was observed only in Bueno and El buenet (both international cultivars).

Among the esters, higher amounts of ethyl-3-OH-butyrate and 2-methyl-butanoic acid were observed.

The very limited presence of C6 alcohols, deriving from the enzymatic activities of lipoxygenase, highlights how loquat is poorly endowed with these enzymes, which lead to the formation of herbaceous aromas that are not always pleasant, or that the sample preparation was done correctly. The different cultivars examined show significant differences in ester and alcohol content: international Algerie and Bueno cultivars tend to have the highest values.

The total contents of acids, aldehydes and benzenoids show a similar profile in most cultivars. Significant differences were recorded for total acid content in Claudia (local cultivar) which represent the highest values (2792 mg/kg flesh fruit) and in Peluche (international cultivar), which represent the lowest values (1245 mg/kg flesh fruit); in total aldehydes, Algerie has significantly higher values and BRT 20, El buenet and Golden nugget are lower; finally, benzenoids are present in higher amounts in Bueno.

Glycosylated volatile compounds

A limited number of glycosylates, released by enzymatic hydrolysis, have been recorded in the studied cultivars, demonstrating that loquat does not have a high supply of sugar-related flavors, which can be released and perceived after swallowing the flesh (flavor).

Among the identified glycosylates, there is a clear predominance of compounds belonging to the class of benzenoids and C13-norisoprenoids followed by terpenes, the latter is present at low concentrations and with significant differences between cultivars.

Among the benzenoids, the presence of eugenol, 4-vinylguaiacol, vanillin, syringaldehyde, methylvanillate, and 2-phenylethanol was shown according to the study outcome of Chen *et al.* (2011) and Shaw and Wilson (1982). Among the C13-norisoprenoids and terpenes presence of vomifoliol and 3-oxo-α-ionol and their dehydroxylated forms is recorded. Important compounds that contribute to aromatic sensations range from fruity to floral (Table 5). The international cultivars tend to have a higher concentration of these compounds, especially Algerie and Golden nugget. Among the local cultivars, Claudia has the highest values. Higher values for total benzenoids are observed in Claudia (local cultivar), Golden nugget, and Algerie (international cultivars); Higher C13-norisoprenoids in Algerie and Golden nugget; the latter also had higher total terpenes. As in all cultivars, the synthesis of terpene compounds is shifted towards dehydroxylated forms (trans-8-Hydroxylinalool and cis-8-Hydroxylinalool), and geraniol is present only among monohydroxylates.

Table 5. Odor descriptor and odor threshold volatile compounds.

Compounds	Odor descriptor	Odor threshold (ppb)	Reference
Terpenes			
Linalool	Floral, lavender	6	Pino and Mesa (2006)
Trans-8-hydroxy-linalool	Sweet, floral, creamy	–	www.thegoodscentscompany.com/
Cis-8-hydroxy-linalool	Sweet, floral, creamy	–	www.thegoodscentscompany.com/
Geranial	Citrus-like, flowery, fruity	32	Pino and Mesa (2006)
C13-norisoprenoids			
3-oxo-a-ionol	Spicy, woody, violet	–	www.pherobase.com
3,4-dihydro-3-oxo-actinidol 1		–	www.pherobase.com
3-OH-b-ionone	Flower, violet	–	www.thegoodscentscompany.com/
Vomifoliol	Fruity	–	www.pherobase.com
Benzenoids			
Eugenol	Clove, spicy, balsamic	6	Pino and Mesa (2006)
4-Vinylguaiacol	Clove, curry	3	Pino and Mesa (2006)
Isoeugenol	Flower	6	Escudero *et al.* (2007)
Methyl vanillate	Caramel, butterscotch, vanilla	990	Escudero *et al.* (2007)
Benzylalcohol	Sweet, flower	–	www.pherobase.com
2-Phenylethanol	Hawthorne, honey, sweet	1100	Pino and Mesa (2006)
Methoxyeugenol	Sweet, flower	–	www.pherobase.com
Syringaldehyde	Sweet, cocoa, chocolate	50,000	Escudero *et al.* (2007)

Conclusion

Among local cultivars, only cv Claudia had higher values of glycosylated compounds highlighting the floral and acidic notes that are appreciated in the market. Regarding the international cultivars, all yellow fleshed cultivars had a higher number of free aromatic compounds that showed cheese and fat notes (butyric and decanoic acid) and other odors and flavors less appreciated by consumers. They have fewer acids and a greater number of glycosylated compounds that showed characteristic floral and woody notes. This article tends to highlight the importance of local and international cultivars in Mediterranean environments that are grown with the best market characteristics.

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